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Effective Hamiltonians derived from equation-of-motion coupled-cluster wave functions: Theory and application to the Hubbard and Heisenberg Hamiltonians

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ABSTRACT
Effective Hamiltonians, which are commonly used for fitting experimental observables, provide a coarse-grained representation of exact many-electron states obtained in quantum chemistry calculations; however, the mapping between the two is not trivial. In this contribution, we apply Bloch’s formalism to equation-of-motion coupled-cluster wave functions to rigorously derive effective Hamiltonians in Bloch’s and des Cloizeaux’s forms. We report the key equations and illustrate the theory by application to systems with two or three unpaired electrons, which give rise to electronic states of covalent and ionic characters. We show that Hubbard’s and Heisenberg’s Hamiltonians can be extracted directly from the so-obtained effective Hamiltonians. By establishing a quantitative connection between many-body states and simple models, the approach facilitates the analysis of the correlated wave functions. We propose a simple diagnostic for assessing the validity of the model space choice based on the overlaps between the target- and model-space states. Artifacts affecting the quality of electronic structure calculations such as spin contamination are also discussed.

I. INTRODUCTION
Coarse graining is commonly used in computational chemistry and physics. It can be deployed in the real space, when a group of atoms is replaced by an effective particle, or in the Hilbert space, when a group of many-body electronic states is represented by a set of states expressed in a compact basis of model states. Coarse-graining is exploited in a number of classic models serving as a foundation of modern solid-state physics: tight binding, Drude–Sommerfeld’s model, and Hubbard’s and Heisenberg’s Hamiltonians. These models explain macroscopic properties of materials through effective interactions whose strengths are treated as model parameters. The values of these parameters are determined either from more sophisticated theoretical models or by fitting to experimental observables.

For example, in Hubbard’s model, the model space comprises configurations obtained by distributing \( N \) electrons over \( M \) sites and each site is represented by just one localized orbital, as illustrated in Fig. 1 for the three-electrons-in-three-centers case. Hubbard’s Hamiltonian includes electron-hopping terms (one-electron transitions facilitated by the couplings between neutral and ionic configurations) described by the parameter \( t \) and the site energies (energies of the ionic configurations) described by the parameter \( U \),

\[
H_{\text{Hub}} = \sum_{i<j} t_{ij} a_{i\sigma} a_{j\sigma} + U \sum_{i} n_{i\alpha} n_{i\beta},
\]  

where indices \( i, j \) denote localized orbitals, \( \sigma \) denotes spin part \( \alpha \) or \( \beta \), operators \( a_{i\sigma}^{\dagger} \) and \( a_{i\sigma} \) are the creation and annihilation operators of an electron on a localized orbital \( i \) with spin \( \sigma \), and \( n_{i\sigma} \) is a particle number operator, \( n_{i\sigma} = a_{i\sigma}^{\dagger} a_{i\sigma} \). While the configurational space in Hubbard’s model is the same as in the complete-active space wave function (using the same orbital space), the two models are not the same: Eq. (1) does not admit two-electron interactions, such...
as direct exchange terms that couple first three configurations from Fig. 1. Although Hubbard’s model parameterizes only one-particle interactions between the configurations, it includes the Coulomb repulsion $U$ between the conducting (active) electrons, making it sufficiently flexible to describe non-trivial physical phenomena, such as Mott–Hubbard’s phase transition.\(^1\)

Heisenberg’s model\(^10\) describes the interaction between open-shell configurations in terms of local spin (an effective quantity that we discuss below). This model is most commonly used to describe magnetic properties of solids.\(^12\) It can be written as

$$H_{\text{Heis}} = - \sum_{A \neq B} J_{AB} S_A S_B,$$

where $A, B$ enumerate radical (or magnetic) centers, $J_{AB}$ is an effective exchange constant, and $S_A$ is an effective localized spin operator associated with center $I$. Heisenberg’s Hamiltonian can be derived from Hubbard’s Hamiltonian through degenerate\(^1\) and canonical perturbation theories;\(^14\) thus, it can be considered an effective theory with respect to Hubbard’s model. Although Heisenberg’s model space does not admit ionic configurations, their effect is folded into the effective exchange parameters.

Effective Hamiltonian theory provides a powerful framework for a rigorous construction of effective Hamiltonians from multiconfigurational many-electron wave functions computed \textit{ab initio}. Pioneering works of Kato,\(^1\) Okubo,\(^16\) Bloch,\(^17\) and des Cloizeaux\(^18\) have established the foundations of the operator effective Hamiltonian theory. Further development came from Löwdin’s partitioning\(^19\) technique, Feshbach’s formalism,\(^20\) and generalizations.\(^21\)–\(^25\) The history and recent developments of effective Hamiltonian theories are summarized in comprehensive reviews.\(^26\)–\(^29\)

Effective theories fulfill a dual role. On one hand, they can be used to develop new electronic structure methods with the systematically improved description of effective Hamiltonians. For example, perturbative construction of the wave operator and effective Hamiltonians has been exploited in the development of various multireference perturbative\(^30\)–\(^32\) and coupled-cluster\(^33\)–\(^39\) methods. On the other hand, effective theories can be used as an interpretation tool by providing an essential description of the complex electronic structure.

The distinction between using effective Hamiltonians for analysis of the electronic structure and method development is not always binary. For example, introduction of Hubbard’s repulsion term $U$ into a density functional expression allowed Anisimov and co-workers to develop a widely used DFT+$U$ method.\(^3\)–\(^15\) Mayhall and Head-Gordon noted that effective exchange couplings $J$ from a single spin-flip (SF) calculation agree with the couplings extracted from more computationally expensive $n$-SF calculations,\(^46\) which led to the development of an effective computational scheme for strongly correlated systems exploiting a coarse-graining idea.\(^17\) In Mayhall’s protocol, a single spin-flip calculation is performed first. Then, under the assumption of Heisenberg’s physics, the exchange couplings are extracted, and an effective Hamiltonian is constructed to compute the spin states that are not accessible in the single spin-flip calculation.

The parameters of effective Hamiltonians also can be obtained indirectly. Experimentally, exchange couplings can be extracted from the temperature dependence of magnetic susceptibility, electron paramagnetic resonance, and neutron scattering experiments.\(^38\)–\(^44\) Theoretically, if there are known relations between the states of interest, such as the Landé interval rule,\(^45\) advanced electronic structure methods can be easily applied.\(^46\) Even more indirectly, exchange couplings can be extracted from contaminated solutions\(^47\) obtained in broken-symmetry density functional theory (BS-DFT) or broken-symmetry coupled-cluster\(^48\) calculations.

Numerous studies\(^49\)–\(^52\) have used Bloch’s and des Cloizeaux’s formalisms to build Heisenberg’s and Hubbard’s effective Hamiltonians from configuration interaction (CI) wave functions. In this contribution, we apply Bloch’s formalism to the equation-of-motion coupled-cluster (EOM-CC) wave functions to rigorously derive effective Hamiltonians in Bloch’s and des Cloizeaux’s forms. We report the key equations and illustrate the theory by examples of systems with several unpaired electrons, giving rise to electronic states of covalent and ionic characters. Our goal is to establish a rigorous mapping between the EOM-CC solutions and effective Hamiltonians and to provide a theoretical basis for the extraction of effective parameters from the EOM-CC calculations. These parameters can be directly compared with the parameters extracted from experimental measurements, facilitating unambiguous comparison between the theory and experiment. In addition, such a mapping provides physical insights into the complex electronic structure of strongly correlated systems. Finally, the theoretical developments presented here serve as a stepping stone toward the development of coarse-grained models of electron correlation in large systems, following Mayhall’s and Head-Gordon’s ideas.
The structure of this paper is as follows: In Sec. II, we provide an overview of the EOM-CC theory and Bloch’s formalism. We then apply Bloch’s formalism to the EOM-CC wave functions and derive the working expressions. Next, we consider several molecules for which we discuss Hubbard’s and Heisenberg’s Hamiltonians rigorously constructed from the EOM-SF-CCSD solutions. Whenever possible, we compare the results from extraction through the Landé rule and from the effective Hamiltonians.

II. THEORY

A. Equation-of-motion coupled-cluster theory

Similar to CI, EOM-CC methods\textsuperscript{53–56} utilize linear parameterization of the wave function,

\[ |\Psi^T_I\rangle = \hat{R}_I|\Phi_0\rangle, \tag{3} \]

\[ |\Psi^T_I\rangle = \langle\Phi_0|\hat{L}^\dagger_I, \tag{4} \]

where \( \Psi_I \) is an EOM target state, \( \hat{R} \) and \( \hat{L} \) are general excitation operators, and \( \Phi_0 \) is the reference determinant, which defines the separation between occupied and virtual orbital spaces. The equations for the amplitudes of the EOM operators are derived variationally, leading to a CI-like eigenproblem.\textsuperscript{57} In contrast to CI, the EOM theory employs a (non-Hermitian) similarity-transformed Hamiltonian,

\[ \hat{H} = e^{-\hat{H}}\hat{H}e^{\hat{H}}, \tag{5} \]

where \( \hat{T} \) is an excitation operator. Because \( \hat{H} \) has the same spectrum as the bare Hamiltonian regardless of the choice of \( \hat{T} \), solving the EOM eigenproblem in the full configurational space, i.e., when \( \hat{R} \) includes all possible excitations, recovers the exact (full CI or FCI) limit. In practical calculations, these operators are truncated, most often to single and double excitations, giving rise to EOM-CCSD ansatz, and the choice of the operator \( \hat{T} \) becomes important. For example, choosing \( \hat{T} = 1 \) leads to plain CISD (CI with singles and doubles), but taking \( \hat{T} \) from the coupled-cluster equations for the reference state amounts to including correlation effects and ensures size-intensivity. Most often, \( \hat{T} \) is truncated at the same level as \( \hat{R} \); for example, in EOM-CCSD, one uses

\[ \hat{T} = \sum_{ia} c^a_i b^i_a + \frac{1}{4} \sum_{ijab} c^a_i c^b_j c^b_j b^i_a b^j_i + \ldots, \tag{6} \]

where \( i, j, \ldots \) and \( a, b, \ldots \) denote occupied and virtual (with respect to \( \Phi_0 \) orbitals. When \( \hat{T} \) satisfies the CC equations, then the reference determinant \( \Phi_0 \) is also an eigen-state of \( \hat{H} \).

Because \( \hat{H} \) is non-Hermitian, the left and right EOM eigenstates are not Hermitian conjugates of each other,

\[ \hat{H}\hat{R}_I|\Phi_0\rangle = E_I|\hat{R}_I|\Phi_0\rangle, \tag{7} \]

\[ \langle\Phi_0|\hat{L}^\dagger_I\hat{H} = \langle\Phi_0|\hat{L}^\dagger_I E_I, \tag{8} \]

but are often chosen to form a biorthogonal set,

\[ \langle\Phi_0|\hat{L}^\dagger_I \hat{R}_I|\Phi_0\rangle = \delta_{II}. \tag{9} \]

Because the excitation operators \( \hat{T} \) and \( \hat{R} \) commute, one can also write the EOM states as

\[ |\Psi^R_I\rangle = \hat{R}_I|\Psi^T_{CC}\rangle, \tag{10} \]

where

\[ |\Psi^T_{CC}\rangle = e^{\hat{T}}|\Phi_0\rangle. \tag{11} \]

This form shows clearly that the EOM-CC states include higher excitations than the respective CI states by virtue of the wave operator \( e^{\hat{T}} \) and that the EOM states are excited states with respect to the reference-state CC wave function. Note that in the derivations below we use EOM states as defined by Eqs. (3) and (4) rather than (10) and (11).

Different choices of \( \hat{R} \) allow access to different manifolds of target states, giving rise to a variety of EOM-CC methods.\textsuperscript{58–61} Common choices include excitation, “spin-flip,” ionization,\textsuperscript{62,63} or electron-attachment\textsuperscript{64} operators. For example, spin-flip operators are

\[ \hat{R}^{SF} = \sum_{ia} c^a_i a^i_a + \frac{1}{4} \sum_{ijab} c^a_i c^b_j c^b_j a^i_a b^j_i + \ldots, \tag{12} \]

\[ \hat{L}^{SF} = \sum_{ia} c^a_i a^i_a + \frac{1}{4} \sum_{ijab} c^a_i c^b_j c^b_j a^i_a b^j_i + \ldots, \tag{13} \]

where the number of creation operators corresponding to \( a \) orbitals is not equal to the number of annihilation operators corresponding to \( a \) orbitals, giving rise to a non-zero \( M_S \) (spin-projection) of \( \hat{R} \) (in contrast, the EOM-EE operators are of the \( M_S = 0 \) type).

B. Effective Hamiltonians

1. General formalism

Effective theories operate with target (large) and model (small) spaces, as illustrated in Fig. 2. Both spaces describe the same set of eigenstates, but using different sets of configurations. The target space contains long multiconfigurational expansions, i.e., it can be a full Hilbert space of a many-body system. The model space contains expansions over a small set of configurations.

![Diagram](https://example.com/diagram.png)

**FIG. 2.** Target and model spaces are connected through a wave operator \( \Omega^{-1} \). The target space can be the full configurational (i.e., Hilbert) space of the system, while the model space is a subspace of the full configurational space.
Bloch’s theory usually starts from target states, which are eigenvectors of the Hermitian Hamiltonian,

\[ H|\Psi_\mu\rangle = E_\mu |\Psi_\mu\rangle, \tag{14} \]

and

\[ P = \sum_\mu |\Psi_\mu\rangle N_\mu^{-2} \langle\Psi_\mu|. \tag{15} \]

Here, the eigenstates \( \Psi_\mu \) are not necessarily normalized to one. \( P \) denotes a projector onto the target space, \( N_\mu \) is the normalization factor of the eigenstate \( |\Psi_\mu\rangle \), \( E_\mu \) is the energy of \( |\Psi_\mu\rangle \), and \( n \) is the dimension of the target space. The selection of the eigenstates in the target space is determined by the problem at hand—we include only those eigenstates that are relevant to a specific physics. The number of states included in the model space (i.e., the dimension of the model space) is the same as that in the corresponding target space. Effective Hamiltonians are defined in the model space such that, by construction, their eigenvalues reproduce the eigenvalues of the target-space Hamiltonian,

\[ H^{\text{eff}}|\tilde{\Psi}^\mu\rangle = E_\mu |\tilde{\Psi}^\mu\rangle, \tag{16} \]

where \( |\tilde{\Psi}^\mu\rangle \) and \( |\Psi^\mu\rangle \) are right and left eigenstates of the effective Hamiltonian, and \( P_0 \) is the projector onto the model space. In other words, the idea behind the effective Hamiltonian entails the transformation of the interaction between the model vectors to reproduce the energies in the target space. The model space is connected to the target space through a wave operator \( \Omega \),

\[ |\tilde{\Psi}^\mu\rangle = \Omega |\Psi^\mu\rangle. \tag{18} \]

The relations (14)–(18) lead to generalized Bloch’s equation, establishing a connection between the wave operator and the effective Hamiltonian,

\[ H\Omega P_0 = \Omega P_0 H^{\text{eff}} P_0. \tag{19} \]

Effective Hamiltonians in Eq. (16) are defined up to a similarity transformation. Therefore, a constraint is needed for a unique definition. Bloch’s constraint (which we denote through a subscript “\( B \)”), also known as intermediate normalization, is

\[ P_0 \Omega_0 P_0 = P_0. \tag{20} \]

This constraint leads to the following expressions for the wave operator and effective Hamiltonian:

\[ \Omega_B = P_0 (P_0 P_0)^{-1} \quad \text{(only in subspaces)}, \tag{21} \]

\[ H^{\text{eff}} = P_0 H^{\text{eff}} P_0 = P_0 H_0 \Omega_B P_0. \tag{22} \]

Equations (21) and (22) mean that if the exact eigen-states and eigen-energies are known, one can select a model space, compute the projectors (and, consequently, the wave operator), and construct \( H^{\text{eff}} \), which, by construction, will yield the same eigen-energies as \( H \).

As an interesting example of an effective theory, one can consider coupled-cluster theory. The exponential operator \( e^{\hat{T}} \) with untruncated \( \hat{T} \) has the meaning of the wave operator connecting the model space (a single Slater determinant) with the exact (FCI) space. Coupled-cluster equations require that the reference determinant \( \Phi_0 \) is the eigenfunction of the effective Hamiltonian \( \hat{H} \),

\[ |\Phi_0\rangle \xrightarrow{\Omega} |\Phi_{CC}\rangle = |\Phi_0\rangle. \tag{23} \]

Thus, \( e^{\hat{T}} \) maps the exact many-body ground state into a single Slater determinant.

Bloch’s effective Hamiltonian is not Hermitian, which may not be convenient for the analysis. Des Cloizeaux gave a recipe for producing a Hermitian effective Hamiltonian \( \hat{H}^{\text{eff}} \) by means of symmetric orthogonalization of Bloch’s eigenvectors. An arbitrary Hermitian effective Hamiltonian can be obtained from Bloch’s effective Hamiltonian through a similarity transformation \( A \). For any Bloch’s eigenprojector, this can be written as

\[ A^{-1} |\tilde{\Psi}^\mu_{R\mu}\rangle = |\tilde{\Psi}^\mu_{H\mu}\rangle E_{\mu} \langle\tilde{\Psi}^\mu_{H\mu}|, \tag{24} \]

\[ A^{-1} |\tilde{\Psi}^\mu_{R\mu}\rangle = |\tilde{\Psi}^\mu_{H\mu}\rangle, \tag{25} \]

\[ \langle\tilde{\Psi}^\mu_{R\mu}|A = \langle\tilde{\Psi}^\mu_{H\mu}|, \tag{26} \]

\[ |\tilde{\Psi}^\mu_{R\mu}\rangle = A A^{-1} |\tilde{\Psi}^\mu_{R\mu}\rangle, \tag{27} \]

Since Bloch’s eigenvectors are biorthogonal,

\[ A A^{-1} = \sum_\mu |\tilde{\Psi}^\mu_{R\mu}\rangle \langle\tilde{\Psi}^\mu_{R\mu}|, \tag{28} \]

\[ \left(A A^{-1}\right)^{-1} = \sum_\mu |\tilde{\Psi}^\mu_{R\mu}\rangle \langle\tilde{\Psi}^\mu_{R\mu}|. \tag{29} \]

\( A \) is defined up to a unitary transformation. Polar decomposition of a matrix gives unique positive-semidefinite Hermitian matrix \( P \) and a unitary part \( U \),

\[ A = P U, \]

\[ P = (A A^{-1})^{1/2}. \tag{30} \]

To make the Hermitian effective Hamiltonian physically close to Bloch’s effective Hamiltonian, one has to minimize the degree of unitary rotations, i.e., consider only the square root \((A A^{-1})^{1/2}\). It is easy to show (see the Appendix) that, similar to Löwdin’s symmetric orthogonalization, this transformation changes the eigenvectors to a minimal possible extent.

### 2. Effective Hamiltonians from EOM-CC

Here, we treat the EOM-CC space as the target space: \( |\Psi^\mu\rangle = \tilde{R}_\mu |\Phi_0\rangle \) and \( |\tilde{\Psi}^\mu_{R\mu}\rangle = (\Phi_0)\tilde{L}_\mu^{\dagger} \). Our model space depends on a problem and will be defined for each specific case; it will contain a subset of single EOM-CC amplitudes. The interaction between the configurations in this target space is described through \( \hat{H} \). After substitution into Eq. (22) and cancellation of the normalization prefactors, the final expressions are

\[ I_{\mu',\mu''} = \sum_\mu \langle\Phi_\mu|\tilde{\Psi}^\mu_{R\mu}\rangle \langle\tilde{\Psi}^\mu_{R\mu'}|\Phi_\mu''\rangle, \tag{31} \]
\[ H_{\text{eff}}^{\mu} = \sum_{\nu \neq \mu} |\Phi_\nu \rangle \langle \Phi_\nu | \sum_{\mu'} |\Psi^\mu_\nu \rangle E_{\mu'} |\Psi^{\mu'}_{\mu} \rangle \left( \Gamma^{-1} \right)_{\mu' \mu} |\Phi_{\mu'} \rangle. \] (32)

Here, we assumed that the model functions \( \Phi_i \) are orthonormal. Eigenfunctions of Bloch’s Hamiltonian are

\[ |\Psi^\mu \rangle = \sum_\nu |\Phi_\nu \rangle \langle \Phi_\nu | |\Psi^\mu_\nu \rangle, \] (33)

\[ \langle \Psi^\mu \rangle = \sum_{\mu'} \langle \Psi^\mu \rangle_{\mu'} |\Phi_{\mu'} \rangle. \] (34)

Assuming that \( \langle \Phi_\nu | \Psi^\mu_\nu \rangle \) and \( \langle \Psi^\mu \rangle_{\mu'} |\Phi_{\mu'} \rangle \) are invertible, one can get biorthogonality of Bloch’s eigenstates,

\[ L_{\text{EOM}} R_{\text{EOM}} = I, \] (35)

where columns of \( R_{\text{EOM}} \) and \( L_{\text{EOM}} \) are Bloch’s eigenvectors in the basis of model functions and columns of \( R_{\text{EOM}} \) and \( L_{\text{EOM}} \) are overlaps of the EOM vectors with model functions \( \langle \Phi_\nu | \Psi^\mu \rangle \) and \( \langle \Phi_\nu | \Psi^\mu \rangle \). This relation reveals the physical meaning of \( I \), it is a metric tensor for the EOM vectors projected onto the model space; thus, it quantifies how well the model states can represent the target states. This observation suggests using the overlaps (specifically, the lowest absolute value of the eigenvalues of \( I \)) as a diagnostic of whether a particular model space is capable of accurate representation of the given target space.

Des Cloizeaux’s transformation is obtained in a similar way,

\[ A A^T = R_{\text{EOM}} R_{\text{EOM}}^T, \] (36)

\[ A_C = (A A^T)^{1/2}, \] (37)

where \( A \) denotes similarity transformation \( A \) in a basis of orthonormal model functions.

III. NUMERICAL EXAMPLES AND DISCUSSION

A. Computational details

We implemented the tools for constructing the effective Hamiltonians from the EOM-CC wave functions within the Q-Chem package.61,62,72 The illustrative examples in this work use EOM-SFCCSD,61 but the same workflow can be executed with other EOM-CC methods. Briefly, the computational procedure follows:

1. Perform an SCF calculation for a high-spin reference state.
2. Determine single occupied orbital space by computing corresponding \( \alpha \) and \( \beta \) orbitals by means of singular value decomposition (SVD) of the \( \alpha \beta \) block of the overlap matrix.
3. Localize orbitals within singly occupied space.
4. (Optional) Apply the open-shell frozen natural orbital approximation (OSFNO)’ in the virtual space.
5. Construct the model space using an appropriate subset of EOM-CC amplitudes (see Secs. III D and III E for specific examples).
6. Build effective Hamiltonians in Bloch’s and des Cloizeaux’s forms from the EOM-CC energies and relevant amplitudes, as described above.

The validity of the selected model space can be assessed by considering the overlaps between the target and model spaces. Once the effective Hamiltonian is computed, one can extract parameters of Hubbard’s or Heisenberg’s Hamiltonians and assess the validity of these models. Here, we considered non-relativistic EOM-CC calculations. The algorithm can be generalized to include perturbative treatment of spin–orbit couplings46 to enable the extraction of other magnetic properties, such as magnetic anisotropies. Additional details of the algorithm are given below; an example of an input is provided in the supplementary material.

To illustrate the theory, we constructed effective Hamiltonians for four representative molecules (structures are shown in Fig. 3) with two and three strongly correlated electrons (i.e., diradicals68 and triradicals69):

**Hubbard’s model:** propane-1,3,5-triyi (molecule 1) and pentane-1,3,5-triyi (molecule 2). These molecules are examples of organic di- and triradicals.

**Heisenberg’s Model:** PATFIA (magnet 1, Ref. 71) and tris-(3-acetylamino-1,2,4-triazolate) motif of HUKDOG (magnet 2, Ref. 72). These systems are examples of single molecule magnets (SMMs)—they can also be described as di- and tri-radicals, but with metallic radical centers. The geometry of magnet 1 optimized with \( \omega \)B97X-D/cc-pVTZ for the triplet state was taken from Ref. 46. As in Ref. 46, the ferrocene group was not included in the calculations. We also excluded water molecules, sulfate groups, and perchlorate anions in the structure of magnet 2. The geometry of magnet 2 was optimized with \( \omega \)B97X-D/cc-pVTZ and is given in the supplementary material.

We optimized the geometry of magnet 2 with finite thresholds: \( 10^{-3} \) tolerance on the maximal gradient component (a.u.) and \( 10^{-6} \) a.u. on the energy change; these thresholds are tighter than those defined in Q-Chem’s default criteria for geometry optimization. The resulting geometry is slightly asymmetric within these criteria (for example, Cu–Cu distances are 3.416, 3.420, and 3.418 Å). Tighter thresholds lead to a symmetric geometry. The C3 symmetry point group has degenerate irreducible representations, which leads to problems with degenerate EOM solutions, as described in Ref. 68. To circumvent these problems, we used the

![FIG. 3. Structures of the considered systems. Color code: copper (bronze), nitrogen (blue), oxygen (red), carbon (gray), and hydrogen (white). In molecule 1 and molecule 2, representing organic di/triradicals, the unpaired electrons are localized on the odd carbon atoms. In single-molecule magnets (magnet 1 and magnet 2), the unpaired electrons are localized on the copper centers.](image-url)
lower symmetry geometry, which we also provide in the supplementary material. In this non-symmetric geometry, the doublet states are split by only 2.5 cm$^{-1}$.

In the SMM calculations, we used EOM-SF-CCSD with OSFNO truncation of the virtual space with the total population threshold of 99%. We used the single precision$^{65,66}$ capability of the libxmn tensor contraction library$^{67}$ in calculations of copper SMMs. Unrestricted Hartree–Fock references were used in all correlated calculations. Core electrons were frozen. All calculations were performed with the Q-Chem software.$^{51,53,66}$

B. Model space selection

Starting from a high-spin reference determinant, we define the open-shell orbitals through SVD of the overlap matrix of an occupied and $\beta$ virtual spin-orbitals, as in the OSFNO scheme$^{62}$ and in Ref. 37. The singular vector pairs corresponding to open-shell $\alpha$ and $\beta$ spin-orbitals have near unity singular values. All other singular values are zero (ROHF) or small (UHF), enabling the separation of the open-shell subspace. This is followed by the localization of open-shell orbitals. Here, we used Foster–Boys’ localization criterion$^{75}$ and in Ref. 37. The model spaces were generated by one-electron spin-flipping excitations acting on the reference determinant and constrained to open-shell subspaces. For Heisenberg’s model space, we considered only open-shell determinants, while for Hubbard’s model space, we also included ionic determinants (shown in Fig. 1).

C. Extraction of parameters from effective Hamiltonians

To construct Heisenberg’s Hamiltonian, one should first compute the effective Hamiltonian using the model space with open-shell configurations only (see Fig. 1). Then, the parameters for Heisenberg’s model ($J_{AB}$) are given by the sum of matrix element pairs between the respective configurations.

For Hubbard’s Hamiltonian, the model space should include both open-shell and ionic configurations. Once the effective Hamiltonian is constructed, the extraction of the parameters is also rather straightforward. A simple relation between the matrix elements and effective parameters is established by the substitution of Hubbard’s Hamiltonian definition and second quantization algebra. Let $A$ and $B$ subscripts denote radial centers $A$ and $B$, $CS$ and $OS$ denote closed-shell and open-shell determinants, and $REF$ denotes a high-spin reference state (in this example, it is a high-spin triplet state). The expressions for the diagonal and off-diagonal matrix elements are

\[
\langle CS_A | H_{Hub} | CS_A \rangle = \langle CS_A | U \sum \sigma n_{\alpha B} \sigma | CS_A \rangle = U \langle CS_A | (1 + 0) | CS_A \rangle = U, \tag{38}
\]

\[
\langle CS_A | H_{Hub} | OS_A \rangle = \langle CS_A | \sum_{i,j} t_{ij} a_{i\alpha}^\dagger a_{j\beta} | OS_A \rangle = U \langle REF | (a_{i\alpha}^\dagger a_{j\beta}) (\sum_{i,j} t_{ij} a_{i\alpha}^\dagger a_{j\beta}) | REF \rangle = \langle REF | (a_{i\alpha}^\dagger a_{j\beta}) a_{i\sigma}^\dagger a_{j\sigma} | REF \rangle = -t_{i\alpha j\beta}. \tag{39}
\]

D. Hubbard’s effective Hamiltonian

Localized orbitals (shown in Fig. 4 and Fig. S1) enable unequivocal identification of covalent or ionic character of the electronic configurations constructed from these orbitals. Bloch’s and des Cloizeaux’s effective Hamiltonians for molecules 1 and 2 built for covalent and ionic configurations from EOM-SF-CCSD/cc-pVTZ are shown in Fig. 4 and Eqs. (S1)–(S3) in the supplementary material. We note that des Cloizeaux’s transformation either does not change the matrix elements of the effective Hamiltonian on the diagonal (molecule 1) or alter them in a minimal way (molecule 2). Des Cloizeaux’s transformation averages the off-diagonal matrix elements yielding a Hermitian effective Hamiltonian. The validity of the selected model spaces is reflected by the weights of the leading configurations shown in Table S1 in the supplementary material and by the smallest eigenvalue of metric tensor $I$. For molecule 1, it is 0.76, confirming that the selected model space adequately represents the chosen set of the target states. For molecule 2, we obtain a smaller value (0.45), suggesting that some of the selected states are represented not as well as the states in molecule 1.

The obtained matrix elements of effective Hamiltonians directly correspond to the coupling parameters in Hubbard’s Hamiltonian, as explained in Sec. III C. In particular, the elements corresponding to hopping coupling $t$ and energies of ionic configurations $U$ [see Eq. (39)] are shown in blue in Fig. 4. However, Hubbard’s model does not include two-electron couplings, such as an effective direct exchange between the open-shell determinants and effective interaction between the ionic determinants. The singlet–triplet gap (EOM-SF-CCSD/cc-pVTZ) between the two lowest states in molecule 1 is 0.077 eV; by construction, it is reproduced exactly by Bloch’s and des Cloizeaux’s effective Hamiltonians. The contribution of the ionic configurations and the validity of Hubbard’s model are revealed by the magnitudes of the matrix elements of effective Hamiltonians. The truncated (inexact) effective Hamiltonian, including only open-shell determinants (Fig. 4), gives the singlet–triplet gap of 0.084 eV. This observation can also be rationalized from perturbative arguments: the effective direct exchange splits the open-shell states in the first order of degenerate perturbation theory. The indirect exchange from the ionic configurations comes only from the second-order perturbation, having a magnitude of $0.1^2/4 = 2.5 \cdot 10^{-3}$ eV, which is by one order of magnitude smaller than the one in molecule 1.
smaller than the direct exchange. This analysis reveals the nature of interaction of open-shell configurations in this system: the singlet–triplet gap primarily comes from the effective direct exchange, rather from the interaction with the ionic configurations. The standard Hubbard Hamiltonian (blue numbers in Fig. 4) does not include these interactions; consequently, its diagonalization yields a poor value of the singlet–triplet gap (~0.008 eV—wrong magnitude and sign). To accommodate this physics, Hubbard’s Hamiltonian can be extended to include the direct exchange contribution, as was done in Ref. 52.

It is instructive to compare the open-shell sub-block of this effective Hamiltonian with Heisenberg’s Hamiltonian constructed considering only open-shell configurations [shown in the supplementary material, Eqs. (S4) and (S5)]. By construction, this Hamiltonian yields exactly the same singlet–triplet gap as the one constructed using Hubbard’s model space. The coupling matrix elements give the values of effective exchange constants $J$, which include all many-body effects present in the EOM-SF-CCSD wave functions. These effects include the contributions of the ionic configurations, which are treated explicitly in the case of Hubbard’s model space. The difference between the OS–OS couplings from Heisenberg’s Hamiltonian ($0.038$ eV) and the matrix elements between the OS configurations from the Hamiltonian constructed using Hubbard’s space ($0.042$ eV) quantify the contribution of the ionic configurations into the effective $J$ values. Finally, the lowest absolute eigenvalue of $I$ is $0.96$, meaning that Heisenberg’s model captures low-energy physics in molecule 1 very well.

The considered triradical—molecule 2—exhibits similar trends and similar effective interaction constants shown in Eqs. (S2) and (S3) and Fig. S1. Although all the energies in Bloch’s and des Cloizeaux’s effective Hamiltonians have been shifted to produce a zero trace in the open-shell submatrix, the individual energies of the open-shell determinants are not zero. This is likely due to some degree of spin contamination of the EOM-SF-CCSD states used to build the effective Hamiltonians. Spin contamination is especially large in the highest ionic states: the corresponding $\langle S^2 \rangle$ values are $1.06$ and $1.17$. This degree of spin contamination can deteriorate the quality of energy, resulting in somewhat higher energies of the corresponding ionic configurations: $6.5$ eV and $6.3$ eV. These configurations are not well represented by the model space, resulting in a relatively small lowest eigenvalue of $I$ of $0.45$, which is smaller than the corresponding value ($0.76$) of molecule 1. We note that there are several spin-contaminated electronic states with lower energies that are not represented well by the model space; these states were not included in the effective Hamiltonian. Interestingly, Heisenberg’s model space for this system [see Eqs. (S6) and (S7) in the supplementary material] shows a much better overlap, with the lowest eigenvalue of $I$ of $0.96$, indicating that open-shell states are described well by this effective Hamiltonian.

**E. Heisenberg’s effective Hamiltonian**

Figures 5 and 6 show localized open-shell orbitals and the effective Hamiltonians constructed from the open-shell determinants expressed using these orbitals. The complex character of the wave functions has been illustrated before, yet the SVD-transformed open-shell orbitals yield a relatively simple expansion of wave functions over this small set of configurations. Open-shell configurations in these orbitals are the dominant configurations contributing more than 90% of the total amplitude sum (Table S2), which confirms the validity of Heisenberg’s model in representing these systems. Our proposed diagnostic values, the lowest absolute eigenvalues of $I$, equal 0.91 and 0.93, which means that the model space represents the target wave functions very well.

We note that by no means, the quality of this compact model space means that the effect of other electronic configurations in the full Hilbert space (e.g., double EOM-SF-CCSD amplitudes) can be neglected. To illustrate this point, we computed the eigenvalues of $H$ in the space of single excitations only, as in EOM-SF-CCSD-S$^2$; the results are shown in Table S3 in the supplementary material. The energy gaps between the target states are reproduced reasonably well (albeit not exactly); however, the resulting states are severely spin-contaminated.

The obtained effective Hamiltonians shown in Figs. 5 and 6 were shifted to achieve a zero trace, as in the case of Hubbard’s Hamiltonian. Although the diagonal elements are small, they deviate from zero by 0.9–2.6 cm$^{-1}$. This artifact is a violation of time-reversal symmetry, which can be explained by a small spin contamination of EOM-SF-CCSD states entering the effective

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**FIG. 5.** Localized open-shell orbitals (left), Bloch’s (right, top), and des Cloizeaux’s (right, bottom) effective Hamiltonians for magnet 1. All matrix elements are in cm$^{-1}$.

**FIG. 6.** Localized open-shell orbitals (left), Bloch’s (right, top), and des Cloizeaux’s (right, bottom) effective Hamiltonians of magnet 2. All matrix elements are in cm$^{-1}$.
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Table I. Exchange coupling constants, $J$ (cm$^{-1}$), extracted from the EOM-SF-CCSD/cc-pVDZ calculations in different ways.

<table>
<thead>
<tr>
<th>Method</th>
<th>Magnet 1</th>
<th>Magnet 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bloch</td>
<td>-70.40</td>
<td>-96.73, -93.61, -97.51</td>
</tr>
<tr>
<td>Des Cloizeaux</td>
<td>-70.40</td>
<td>-96.72, -93.64, -97.50</td>
</tr>
<tr>
<td>Landé rule</td>
<td>-70.47</td>
<td>-95.96</td>
</tr>
</tbody>
</table>

*Here, we used a three-center generalization of the Landé rule:* $E(Q) - E(D) = -\frac{1}{2}J$. Energies of the two doublet states were averaged.

Hamiltonian construction. The effective exchange coupling constants $J$ (shown in Table I) were extracted from the off-diagonal elements of the effective Hamiltonians and through the Landé interval rule. Bloch’s and des Cloizeaux’s forms of effective Hamiltonians predict nearly identical values of $J$, slightly different from the Landé rule. This can be attributed to small non-zero diagonal terms contributing to eigenvalues and entering the energy gaps used in the Landé rule.

IV. CONCLUSION

We generalized Bloch’s formalism to a non-Hermitian Hamiltonian ($\hat{H}$) and presented the application of the resulting theory to the EOM-CC function. We compared Bloch’s and Cloizeaux’s versions of the effective Hamiltonian approach and demonstrated that they perform similarly. The constructed Bloch’s and des Cloizeaux’s effective Hamiltonians provide a direct way to interpret the EOM-CC function in terms of effective theories. The theory is formulated using model spaces built from localized open-shell orbitals computed via SVD of the overlap between the $\alpha$ and $\beta$ HF orbitals (such as in OSFNO). The localization of open-shell orbitals allows one to quantify the ionic and covalent characters of the wave functions. The effective Hamiltonians, which are constructed in a rigorous manner, supply the interaction constants for the model Hamiltonians, such as the Heisenberg and Hubbard Hamiltonians. The physical quality of the selected models can be assessed by considering the eigenvalues of $I$, the matrix that quantifies the overlap between the model and target spaces. We propose to use the lowest absolute eigenvalue of $I$ as a diagnostic in the construction of the effective Hamiltonians. We observe that Hubbard’s model space gives smaller values of the diagnostic than Heisenberg’s model space. This can be attributed to the effect of ionic configurations: the states with ionic character are known to have large dynamic correlation (due to Coulomb repulsion), which leads to more multiconfigurational wave functions and, therefore, reduces the overlap with model spaces. The quality of electronic structure calculations, such as the degree of spin contamination, enters the constructed effective Hamiltonians and affects the respective parameters. In particular, spin contamination leads to a small difference in magnetic exchange couplings extracted in different ways. This work provides a foundation for the direct comparison of the results of many-body calculations with the experimentally derived effective parameters for magnetic systems and for further development of coarse-grained approaches to strong correlation.

SUPPLEMENTARY MATERIAL

See the supplementary material for Hubbard’s Hamiltonian, localized open-shell orbitals of molecule 2, Heisenberg’s Hamiltonians for molecule 1 and molecule 2, leading amplitudes in open-shell orbital subspace and overlaps, ligand impact on $J$ values of magnet 2, relevant Cartesian coordinates, and an example of an input.

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APPENDIX: PROOF OF OPTIMALITY OF DES CLOIZEAUX’S TRANSFORMATION

Let us find a similarity transformation $A$ of Bloch’s effective Hamiltonian such that the eigenvectors of the resulting Hermitian Hamiltonian differ from Bloch’s eigenvectors to a minimal extent. For this purpose, we formulate the problem as the overlap maximization with right and left Bloch’s eigenvectors,

$$
\sum_{\mu} (\langle \Psi_{H,\mu}^{\dagger} | \Psi_{H,\mu}^{\dagger} \rangle + \langle \Psi_{H,\mu} | \Psi_{H,\mu} \rangle) = \sum_{\mu} (\langle \Psi_{H,\mu}^{\dagger} | A^{-1} | \Psi_{H,\mu}^{\dagger} \rangle + \langle \Psi_{H,\mu} | A | \Psi_{H,\mu} \rangle) \rightarrow \text{max}. \quad (A1)
$$

This problem can be viewed as a trace maximization: Find such a unitary matrix $U$ for a given $A$ that maximizes $\text{Tr}(AU) + \text{Tr}(U^{-1}A^{-1})$. Based on singular value decomposition $A = W \Sigma V^\dagger$ and Cauchy–Schwarz inequality, one can prove \(^{1}\) that the maximum of both $\text{Tr}(AU)$ and $\text{Tr}(U^{-1}A^{-1})$ is achieved at $U_{\text{opt}} = VW^\dagger$. Therefore, $AU_{\text{opt}} = W \Sigma V^\dagger V W^\dagger = W \Sigma W^\dagger$, which is the polar part of $A$.

REFERENCES

1. In the condensed matter community, such downfolding of the Hilbert space is often referred to as “low-energy models.”
Most often, Hubbard's models include only the hops between the nearest neighbors, but in this work, we waive this limitation and consider all possible one-electron hops.


